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Reduced Form for Coulomb-wave Multicenter Integrals

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In a previous paper [J. C. Straton, Phys. Rev. A **41**, 71 (1990)] an integro-differential transform was introduced and utilized to obtain the analytically reduced form for multicenter integrals composed of general-state hydrogenic orbitals, Yukawa or Coulomb potentials, and plane waves. The present paper extends this result to include Coulomb waves.

I. INTRODUCTION

Theories within atomic and molecular physics generally lead to multicenter integrals containing products of hydrogenic orbitals, Yukawa or Coulomb potentials, plane waves, and Coulomb waves. In a series of papers[1-5] the author has developed the analytically reduced form for the general case that excludes Coulomb waves. The present paper removes this exclusion. Equations from Refs. 4 and 5 will be referred to by suffixing "-I" and "-II," respectively, to the equation numbers.

II. THE INCLUSION OF COULOMB WAVES

The general multicenter integral to be reduced is

$$S^{\eta_1 j_1 \cdots \eta_M j_M}_{I_1 J_1 \ldots I_M J_M}(\mathbf{p}_1,\ldots,\mathbf{p}_m;\mathbf{y}_1,\ldots,\mathbf{y}_M;\nu_K,\mathbf{Q}_K,\ldots,\nu_M,\mathbf{Q}_M)$$
$$= \int d^3x_1 \cdots d^3x_m e^{-i(\mathbf{p}_1\cdot\mathbf{x}_1+\cdots+\mathbf{p}_m\cdot\mathbf{x}_m)} P^{\eta_1 j_1}_{I_1 J_1}(\mathbf{R}_1)\cdots P^{\eta_{K-1} j_{K-1}}_{I_{K-1} J_{K-1}}(\mathbf{R}_{K-1}) \bar{P}^{\eta_K j_K}_{I_K J_K}(\mathbf{R}_K,\nu_K,\mathbf{Q}_K)$$
$$\times \cdots \bar{P}^{\eta_M j_M}_{I_M J_M}(\mathbf{R}_M,\nu_M,\mathbf{q}_M) \tag{1}$$

where

$$P^{\eta j}_{IJ}(\mathbf{R}) = u_I(\mathbf{R})\ldots u_J(\mathbf{R})V^{\eta j}(\mathbf{R}) \tag{2}$$

and

$$\bar{P}^{\eta j}_{IJ}(\mathbf{R},\nu,\mathbf{Q}) = P^{\eta j}_{IJ}(\mathbf{R})\,{}_1F_1(i\nu,1,i(QR+\mathbf{Q}\cdot\mathbf{R})) \tag{3}$$

in which the u's are hydrogenic orbitals [(14-II)–(16-II)],

$$V^{\eta j}(\mathbf{R}) = R^{j-1}e^{-\eta R}\ , \tag{4}$$

and

$$\mathbf{R}_i = \sum_{j=1}^{m} t_{ij}\mathbf{x}_j + \sum_{j=1}^{M} u_{ij}\mathbf{y}_j\ . \tag{5}$$

For each confluent hypergeometric function, introduce the real-contoured integral transform[6]

$${}_1F_1(a,b,z) = \frac{1}{B(a,b-a)}\int_0^1 e^{z\tau}\tau^{a-1}(1-\tau)^{b-a-1}d\tau\ , \tag{6}$$

which is more amenable to numerical integration than the more commonly used[7-9] complex-contoured transform (containing an identical integrand). It will be shown in Sec. III that the former choice gives the same result as the latter.

The final reduced form of the Coulomb-wave integral is

$$S^{\eta_1 j_1 \ldots n_M j_m}_{I_1 J_1 I_M J_M}(\mathbf{p}_1,\ldots,\mathbf{p}_m;\mathbf{y}_1,\ldots,\mathbf{y}_M;\nu_K,\mathbf{Q}_K,\ldots,\nu_M,\mathbf{Q}_M)$$
$$= \pi^{3m/2}\int_0^\infty d\rho_1\cdots d\rho_M \int_0^1 d\tau_K \tau^{i\nu_K-1}(1-\tau)^{-i\nu_K}$$
$$\times\cdots\int_0^1 d\tau_M\ \tau^{i\nu_M-1}(1-\tau)^{-i\nu_M}\ A^{n_1 j_1}_{I_1 J_1}(\rho_1,\mathbf{q}_1)\cdots A^{n_{K-1} j_{K-1}}_{I_{K-1} J_{K-1}}(\rho_{K-1},\mathbf{q}_{K-1})$$
$$\times\frac{A^{n_K j_K}_{I_K J_K}(\rho_K,\mathbf{q}_K)\prod_{j'=1}^{M} e^{iu_{Kj'}\tau_K \mathbf{Q}_K\cdot\mathbf{y}_{j'}}}{B(i\nu_K,1-i\nu_K)}$$
$$\times\cdots\frac{A^{n_M j_M}_{I_M J_M}(\rho_M,\mathbf{q}_M)\prod_{j'=1}^{M} e^{iu_{Mj'}\tau_M \mathbf{Q}_M\cdot\mathbf{y}_{j'}}}{B(i\nu_M,1-i\nu_M)}\frac{e^{-\Omega/\Lambda}}{\Lambda^{3/2}}\ . \tag{7}$$

The A's are given by [(24-II)–(29-II)],

$$
\begin{aligned}
A_{IJ}^{\eta j}[\rho, i\mathbf{q}] = {} & \frac{e^{-\gamma^2/4\rho}}{2^j\sqrt{\pi}} \left(\sum_{s_I=0}^{n_I-\ell_I-1} \frac{(-1)^{S_I}\,(\lambda_I/n_I)^{s_I+\ell_I}\lambda_I^{3/2}\,N_{n_I\ell_I}}{(n_I-\ell_I-1-s_I)!(2\ell_I+1+s_I)!s_I!} \right. \\
& \left. \times\cdots\times \sum_{s_J=0}^{n_J-\ell_J-1} \frac{(-1)^{s_J}(\lambda_J/n_J)^{s_J+\ell_J}\lambda_J^{3/2}\,N_{n_J\ell_J}}{(n_J-\ell_J-1-s_J)!(2\ell_J+1+s_J)!s_J!} \right) \\
& \times \sum_{L_1=L_{1\,\min}}^{L_{1\,\max}}{}^{(2)} (-1)^{M_{I+1}} \left(\frac{(2\ell_I+1)(2\ell_{I+1}+1)(2L_1+1)}{4\pi} \right)^{1/2} \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ 0 & 0 & 0 \end{pmatrix} \\
& \quad \times \begin{pmatrix} \ell_I & \ell_{I+1} & L_1 \\ m_I & m_{I+1} & -M_{I+1} \end{pmatrix} \\
& \times \sum_{L_2=L_{2\,\min}}^{L_{2\,\max}}{}^{(2)} (-1)^{M_{I+2}} \left(\frac{(2L_1+1)(2\ell_{I+2}+1)(2L_2+1)}{4\pi} \right)^{1/2} \\
& \quad \times \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & \ell_{I+2} & L_2 \\ M_I & m_{I+2} & -M_{I+2} \end{pmatrix} \\
& \times\cdots\times \sum_{L_J=L_{J\,\min}}^{L_{J\,\max}}{}^{(2)} (-1)^{M_J} \left(\frac{(2L_{J-1}+1)(2\ell_J+1)(2L_J+1)}{4\pi} \right)^{1/2} \\
& \quad \times \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_{J-1} & \ell_J & L_J \\ M_{J-1} & m_J & -M_J \end{pmatrix} \\
& \quad \times \left(\frac{2^{L_J} H_{s_I+\ell_I+\cdots+s_J+\ell_J-L_J+j}(\gamma/2\sqrt{\rho})}{\rho^{(s_I+\ell_I+\cdots+s_J+\ell_J-L_J+1+j)/2}}\, \mathcal{Y}_{L_J M_J}(i\mathbf{q}) \right) ,
\end{aligned}
\tag{8}
$$

where

$$M_j = m_I + m_{I+1} + \cdots + m_j \ , \tag{9}$$

$$L_{j\,\max} = L_{j-1} + \ell_j \ , \tag{10}$$

$$\mu_j = \max(|L_{j-1} - \ell_j|, |M_{j-1} + m_j|) \ , \tag{11}$$

and

$$L_{j\,\min} = \begin{cases} \mu_j & \text{if } L_{j\,\max} + \mu_j \text{ is even} \\ \mu_j + 1 & \text{if } L_{j\,\max} + \mu_j \text{ is odd,} \end{cases} \tag{12}$$

and where the index "(2)" on the summation sign indicates that one is to sum in steps of 2.

To account for the Coulomb waves (30-II) must be modified to read

$$
\begin{aligned}
\gamma_j = {} & \lambda_{I_j}/n_{I_j} + \cdots + \lambda_{J_j}/n_{J_j} + \eta_j \\
& + \begin{cases} 0, & j < K \\ -iQ_j\tau_j\, , & j \geq K\ . \end{cases}
\end{aligned}
\tag{13}
$$

As in (36-II) and (34-II)

$$\Lambda = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1m} \\ a_{21} & a_{22} & & a_{2m} \\ \vdots & & \ddots & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mm} \end{vmatrix} \ , \tag{14}$$

where

$$a_{ij} = \sum_{k=1}^{M} \rho_k t_{ki} t_{kj} \ . \tag{15}$$

From (38-II), (35-II), and (42-II)

$$\Omega = C\Lambda + \sum_{i=j}^{m} \sum_{j=1}^{m} \mathbf{b}_i \cdot \mathbf{b}_j (-1)^{i+j+1} \Lambda_{ij} \ , \tag{16}$$

where Λ_{ij} is Λ with the ith row and jth column deleted,

$$C = \sum_{k=1}^{M} \sum_{j=1}^{M} \sum_{j'=1}^{M} \rho_k u_{kj} u_{kj'} \mathbf{y}_j \cdot \mathbf{y}_{j'} \ , \tag{17}$$

and

$$\mathbf{q}_i = \frac{1}{\Lambda} \sum_{i'=1}^{m} \sum_{j'=1}^{m} (-1)^{i'+j'+1} \Lambda_{i'j'} t_{ii'} \mathbf{b}_{i'} \ , \tag{18}$$

in which the only modification for Coulomb waves is (33-II)

$$\mathbf{b}_{i'} = \frac{i\mathbf{p}_{i'}}{2} + \sum_{k=1}^{M} \rho_k t_{ki'} \sum_{j=1}^{M} u_{kj} \mathbf{y}_j - \frac{i}{2} \sum_{j=K}^{M} t_{ji'} \mathbf{Q}_j \tau_j \ . \tag{19}$$

Finally, if the Kth P in (1) contains two ${}_1F_1$ functions, depending on parameters $\nu, \mathbf{Q}$ and $\nu', \mathbf{Q}'$, one must insert

$$\int_0^1 d\tau'_K \, \frac{\tau'^{i\nu'_K-1}(1-\tau')^{-i\nu'_K}}{B(i\nu'_K, 1-i\nu'_K)} \tag{20}$$

in (7), set $\tau_K \mathbf{Q}_K \rightarrow \tau_K \mathbf{Q}_K + \tau'_K \mathbf{Q}'_K$ in the exponential of (7), and in (19), and set $Q_K \tau_K \rightarrow Q_K \tau_K + Q'_K \tau'_K$ in (13).

III. EXAMPLES

Consider the integral

$$S^{\eta j}(\mathbf{p};0;\nu,\mathbf{Q},\nu',\mathbf{Q}') = \int d^3x \, e^{-i\mathbf{p}\cdot\mathbf{x}} x^{j-1} e^{-\eta x} \, {}_1F_1[i\nu, 1, i(Qx+\mathbf{Q}\cdot\mathbf{x})] \, {}_1F_1(i\nu', 1, i(Q'+\mathbf{Q}'\cdot\mathbf{x})) \, . \tag{21}$$

In this spherically symmetric case

$$A^{\gamma j}(\rho, \mathbf{q}) = \frac{e^{-\gamma^2/4\rho}}{2^j\sqrt{\pi}} \, \frac{H_j(\gamma/2\sqrt{\rho})}{\rho^{(1+j)/2}} \, , \tag{22}$$

where

$$\gamma = \eta - i\tau Q - i\tau' Q' \, . \tag{23}$$

Also

$$\Lambda = \rho, \quad \Lambda_{11} \equiv 1 \, , \tag{24}$$

$$C = 0 \, , \tag{25}$$

and

$$\mathbf{b} = \frac{i}{2} \, (\mathbf{p} - \mathbf{Q}\tau - \mathbf{Q}'\tau') \, , \tag{26}$$

so that

$$\Omega = \tfrac{1}{4} \, (p^2 - 2\tau \mathbf{p}\cdot\mathbf{Q} - 2\tau' \mathbf{p}\cdot\mathbf{Q}' + Q^2\tau^2 + 2\tau\tau' \mathbf{Q}\cdot\mathbf{Q}' + \mathbf{Q}'^2\tau'^2) \, . \tag{27}$$

For $j=0$ the ρ integral gives

$$\begin{aligned} S^{\eta 0}&(\mathbf{p};0;\nu,\mathbf{Q},\nu',\mathbf{Q}') \\ &= \frac{4\pi}{B(i\nu, 1-i\nu)\, B(i\nu', 1-i\nu')} \\ &\quad \times \int_0^1 d\tau \, \tau^{i\nu-1}(1-\tau)^{-i\nu} \\ &\quad \times \int_0^1 d\tau' \, \frac{\tau'^{i\nu'-1}(1-\tau')^{-i\nu'}}{(\gamma^2+\Omega)} \, . \end{aligned} \tag{28}$$

The denominator is

$$\gamma^2 + \Omega = D + F\tau \, , \tag{29}$$

where

$$D = \eta^2 + p^2 + 2(-\mathbf{Q}'\cdot\mathbf{p} - i\eta Q')\tau' \equiv 2\alpha + 2\beta\tau' \tag{30}$$

and

$$\begin{aligned} F &= -2(\mathbf{Q}\cdot\mathbf{p} + i\eta Q) - 2(QQ' - \mathbf{Q}\cdot\mathbf{Q}')\tau' \\ &\equiv -2g - 2d\tau' \, . \end{aligned} \tag{31}$$

Then the τ integral gives[10]

$$\begin{aligned} S^{\eta 0}&(\mathbf{p};0;\nu,\mathbf{Q},\nu',\mathbf{Q}') \\ &= \frac{4\pi}{B(i\nu, 1-i\nu')} \int_0^1 d\tau' \, \frac{\tau'^{i\nu'-1}(1-\tau')^{-i\nu'}}{(F+D)^{i\nu} \, D^{1-i\nu}} \, . \end{aligned} \tag{32}$$

Note that if $\nu = 0$, the τ' integral gives

$$S^{\eta 0}(\mathbf{p};0;0,\mathbf{Q},\nu',\mathbf{Q}') = \frac{4\pi}{(2\beta+2\alpha)^{i\nu'}(2\alpha)^{1-i\nu'}} \, , \tag{33}$$

which is the known result[11] since ${}_1F_1(0,b,z) \equiv 1$.

For the general case define

$$\gamma = g - \alpha, \ \delta = d - \beta \, . \tag{34}$$

Then

$$D = 2\alpha \left(1 + \frac{\beta}{\alpha}\,\tau'\right) \equiv 2\alpha(1 - b\tau') \tag{35}$$

and

$$F + D = -2\gamma \left(1 + \frac{\delta}{\gamma}\tau'\right) \equiv -2\gamma(1 - a\tau') \, . \tag{36}$$

Changing variables to

$$t = \tau' \left(\frac{1-a}{1-a\tau'}\right) \, , \tag{37}$$

$$\begin{aligned} S^{\eta 0}(\mathbf{p};0;\nu,\mathbf{Q},\nu',\mathbf{Q}') = {} & \frac{4\pi(2\alpha)^{i\nu-1}(-2\gamma)^{-i\nu}}{B(i\nu', 1-i\nu')} (1-a)^{1-i\nu'-i\nu+i\nu-1} \\ & \times \int_0^1 dt \, t^{-2+i\nu'+1}(1-t)^{-i\nu'}(1-zt)^{i\nu-1}(1-a+at)^{-i\nu'-1+i\nu'+i\nu-i\nu+1} \, , \end{aligned} \tag{38}$$

where

$$z = \frac{b-a}{1-a} = \frac{\alpha\delta - \beta\gamma}{\alpha(\gamma+\delta)} \, . \tag{39}$$

The t integral may be evaluated[12] giving

$$S^{\eta 0}(\mathbf{p};0;\nu,\mathbf{Q},\nu',\mathbf{Q}') = \frac{2\pi}{\alpha}e^{-\pi\nu}\left(\frac{\alpha}{\gamma}\right)^{i\nu}\left(\frac{\gamma+\delta}{\gamma}\right)^{-i\nu'} F(1-i\nu,i\nu',1,z)\,, \tag{40}$$

where the factor $e^{-\pi\nu}$ arises from the identification $(1/-1)^{i\nu} = (-1/(-1)^2)^{i\nu} = (e^{i\pi}/1)^{i\nu}$. This is Nordsieck's result[7] if one sets $\mathbf{Q} \to -\mathbf{p}_1$, $\mathbf{Q}' \to \mathbf{p}_2$, $\mathbf{p} \to -\mathbf{q}$, $\nu \to a_1$, $\nu' \to a_2$, and $\eta \to \lambda$.

Note that the limits of (33) and (40) are well defined for $\eta \to 0$ when factors of $(-1)^{i\nu}$ are properly accounted for.[8] Thus the Gausian transform[13] leading to (8) is well defined in the limit $\mathrm{Re}\gamma \to 0$ for integrals of this type.

IV. CONCLUSION

The analytically reduced form has been found for the general multicenter integral of products of hydrogenic orbitals, Yukawa or Coulomb potentials, plane waves, and Coulomb waves. It has been shown that the introduction of a real-contoured integral transform for the confluent hypergeometric function, which is more amenable to numerical evaluation than the more common complex-contoured integral transform, gives the known analytical result for Nordsieck's integrals.

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[1] J.C. Straton, Phys. Rev. A **35**, 2729 (1987); **37**, 4531 (1988).

[2] J.C. Straton, Phys. Rev. A **39**, 5062 (1989).

[3] J.C. Straton, Phys. Rev. A **39**, 5071 (1989).

[4] J.C. Straton, Phys. Rev. A **39**, 1676 (1989); **40**, 2819 (1989).

[5] J.C. Straton, Phys. Rev. A **41**, 71 (1990).

[6] *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, Natl. Bur. Stand. Appl. Math. Ser. No. 55, edited by M. Abramowitz and I.A. Stegun (U.S. GPO, Washington, D.C., 1972), p. 505, No. 13.2.1.

[7] A. Nordsieck, Phys. Rev. **93**, 785 (1954).

[8] M.R.C. McDowell and J.P. Coleman, *Introduction to the Theory of Ion-Atom Collisions* (North-Holland, Amsterdam, 1970), pp. 364–370.

[9] M. Brauner, J.S. Briggs, and H. Klar, J. Phys. B **22**, 2265 (1989).

[10] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 287, No. 3.198; or W. Grobner and N. Hofreiter, *Integraltafel Zweiter Teil Bestimmte Interale* (Springer-Verlag, Berlin, 1961), p. 175, No. 421.4.

[11] J.P. Coleman, in *Case Studies in Atomic Collision Physics*, edited by M.R.C. McDowell and E.W. McDaniel (North-Holland, Amsterdam, 1969), Vol. 1, pp. 161–163.

[12] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 1040, No. 9.111.

[13] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 340, No. 3, 471(9); or derivatives with respect to b of W. Grobner and N. Hofreiter, *Integraltafel Zweiter Teil Bestimmte Integrale* (Springer-Verlag, Berlin, 1961), p. 66, No. 9c.